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## Chemistry at the Limits of Coordination

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High coordination anion chemistry has developed rapidly in the last decade most notably in the field of binary fluorides. The discovery of a truly anhydrous fluoride source, tetramethylammonium fluoride,  $(\text{CH}_3)_4\text{NF}^1$ , has led to a renaissance in main group chemistry. Tetramethylammonium fluoride is thermally stable, soluble in organic solvents, and surprisingly resistant to powerful oxidizers such as  $\text{ClF}_3$ ,  $\text{BrF}_5$ , and  $\text{IF}_7$ . Many new anions have been synthesized and characterized through the use of this fluoride source.<sup>2-6</sup> However, relatively few dianions have been studied and characterized to date, including  $\text{XeF}_8^{2-}$ <sup>7-10</sup>,  $\text{TeOF}_6^{2-}$ <sup>4</sup>,  $\text{TeF}_8^{2-}$ <sup>5</sup>, and  $\text{MF}_5^{2-}$  ( $\text{M} = \text{As}, \text{Sb}, \text{Bi}$ )<sup>11</sup>. Problems plaguing the study of new dianions include poor solubility in solution, and the equilibrium between the dianion and its monoanion and fluoride precursors. Several new fluorodianions have been synthesized, characterized through vibrational spectroscopy, and compared to theoretical calculations.

The reinvestigation of an original sample of " $\text{Cs}_3\text{IF}_6$ "<sup>12</sup> found strong evidence that the sample is actually a mixture of  $\text{Cs}_2\text{IF}_5$  and  $\text{CsF}$  rather than  $\text{Cs}_3\text{IF}_6$ . This conclusion has been drawn from the fact that the sample had a Raman band pattern very similar to that reported for the recent, structurally characterized  $\text{XeF}_5^-$ <sup>13</sup>. The infrared spectrum and x-ray powder spectrum of " $\text{Cs}_3\text{IF}_6$ " contained bands indicative of large amounts of  $\text{CsF}$ .

The  $\text{IF}_5^{2-}$  dianion can also be formed in acetonitrile at low temperatures through the reaction of tetramethylammonium fluoride and  $\text{IF}_3$ . It can be made either stepwise through the well known  $\text{IF}_4^-$ , or by the reaction of two equivalents of tetramethylammonium fluoride with  $\text{IF}_3$ . Theoretical calculations were carried out at the SCF/ECP level of theory where a minimum was found for the pentagonal planar  $D_{5h}$  structure. The observed vibrational spectra are in excellent agreement with those calculated for pentagonal planar  $\text{IF}_5^{2-}$  and with those found for isoelectronic, pentagonal planar  $\text{XeF}_5^-$ .

The  $\text{IF}_7^{2-}$  dianion has been prepared by several routes in our laboratory. Two routes involve vacuum pyrolyses, which were carried out in sapphire tube reactors. It was first found that heating a mixture of  $\text{KIF}_6 \cdot n\text{IF}_7$  resulted in the formation of  $\text{K}_2\text{IF}_7$  with  $\text{IF}_7$  and  $\text{IF}_5$ . Later, it was found that heating pure  $\text{KIF}_6$  led to  $\text{K}_2\text{IF}_7$  and  $\text{IF}_5$ . The  $\text{IF}_7^{2-}$  dianion can also be synthesized through the reaction of  $(\text{CH}_3)_4\text{NF}$  with  $\text{IF}_5$  in acetonitrile at room temperature. The vibrational spectra of  $\text{K}_2\text{IF}_7$  are very similar to those of the structurally characterized and isoelectronic  $\text{CsXeF}_7^{14}$ , indicating the same  $C_{3v}$  monocapped octahedral structure.

Presently, there are no nine-coordinate main group  $\text{AX}_9$  species known. Theoretical calculations for  $\text{IF}_9^{2-}$  show that a slightly distorted  $D_{3h}$  structure is vibrationally stable. This structure is very reminiscent of the well known  $\text{ReH}_9^{2-15}$  structure. To date, laboratory efforts have not been successful. The reaction of either two or three equivalents of  $\text{CsF}$  with  $\text{IF}_7$  at high temperatures in a monel cylinder under a fluorine

atmosphere has failed. The reactions of  $(\text{CH}_3)_4\text{NF}$  with  $\text{IF}_7$  in cold acetonitrile, either stepwise through  $\text{IF}_8^{2-}$ , or all at once, also were unsuccessful.

$\text{SbF}_5$  and  $\text{BiF}_5$  are strong Lewis acids which react quantitatively with a fluoride ion source forming the well known octahedral  $\text{SbF}_6^-$  and  $\text{BiF}_6^-$  species. From the known existence of  $\text{TeF}_8^{2-}$ <sup>4, 16-17</sup>, whose precursor  $\text{TeF}_6$  has a similar fluoride affinity as  $\text{BiF}_5$ <sup>18</sup>, the formation of  $\text{SbF}_7^{2-}$  and  $\text{BiF}_7^{2-}$  through the reaction of excess  $\text{CsF}$  with the corresponding Lewis acid seemed reasonable. In the case of  $\text{SbF}_5$ , only partial conversion to  $\text{SbF}_7^{2-}$  was achieved with a 2:1  $\text{CsF}/\text{SbF}_5$  reaction mixture. Even using a 3:1  $\text{CsF}/\text{SbF}_5$  ratio, the product still contained some  $\text{CsSbF}_6$ . For Bismuth, it was found that a 2:1 ratio of  $\text{CsF}/\text{BiF}_5$  gave a high conversion to  $\text{Cs}_2\text{BiF}_7$ , but there was still some  $\text{CsBiF}_6$  present. The Raman signals due to  $\text{BiF}_6^-$  diminished by raising the temperature of the reaction to 300 °C. Bismuth pentafluoride reacted smoothly with  $(\text{CH}_3)_4\text{NF}$  at low temperatures in acetonitrile to form the  $\text{BiF}_7^{2-}$  dianion. In the case of  $\text{SbF}_5$ , reaction with a large excess of  $(\text{CH}_3)_4\text{NF}$  in acetonitrile or sulfur dioxide, gave exclusively the  $\text{SbF}_6^-$  anion. The vibrational frequencies for the  $\text{SbF}_7^{2-}$  dianion were calculated at the SCF/ECP level of theory with a minimum being found for the pentagonal bipyramidal  $D_{5h}$  structure. The calculated frequencies and intensities agreed well with the ones found for  $\text{Cs}_2\text{SbF}_7$ . The vibrational frequencies for the  $\text{BiF}_7^{2-}$  dianion were calculated at the HF level of theory using DZP(F) and ECP/DZP(Bi) basis sets, which also found a minimum for the pentagonal bipyramidal  $D_{5h}$  structure. Again, the calculated frequencies and intensities agreed well with the observed ones.

In summary, several new doubly charged anions,  $\text{IF}_5^{2-}$ ,  $\text{IF}_7^{2-}$ ,  $\text{SbF}_7^{2-}$ , and  $\text{BiF}_7^{2-}$  have been prepared and characterized.  $\text{IF}_5^{2-}$  and  $\text{IF}_7^{2-}$  are only the second known examples of a pentagonal planar  $\text{AX}_5\text{E}_2$  and a monocapped octahedral main group  $\text{AX}_7\text{E}$  species, respectively.  $\text{BiF}_7^{2-}$  and  $\text{SbF}_7^{2-}$  are the first examples of seven coordinate  $\text{AX}_7$  pnictogens, and both dianions adopt a pentagonal bipyramidal structure.

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